

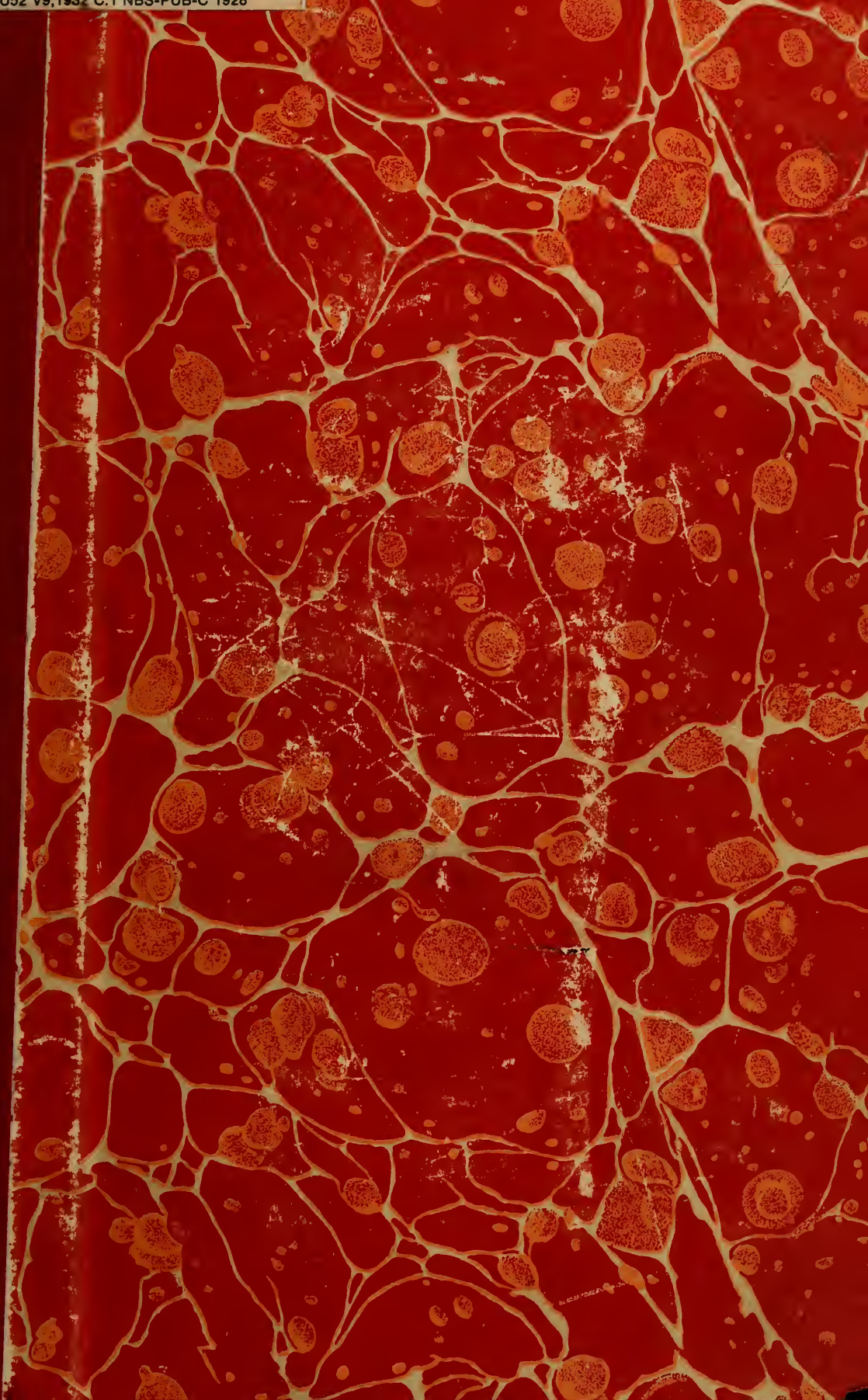
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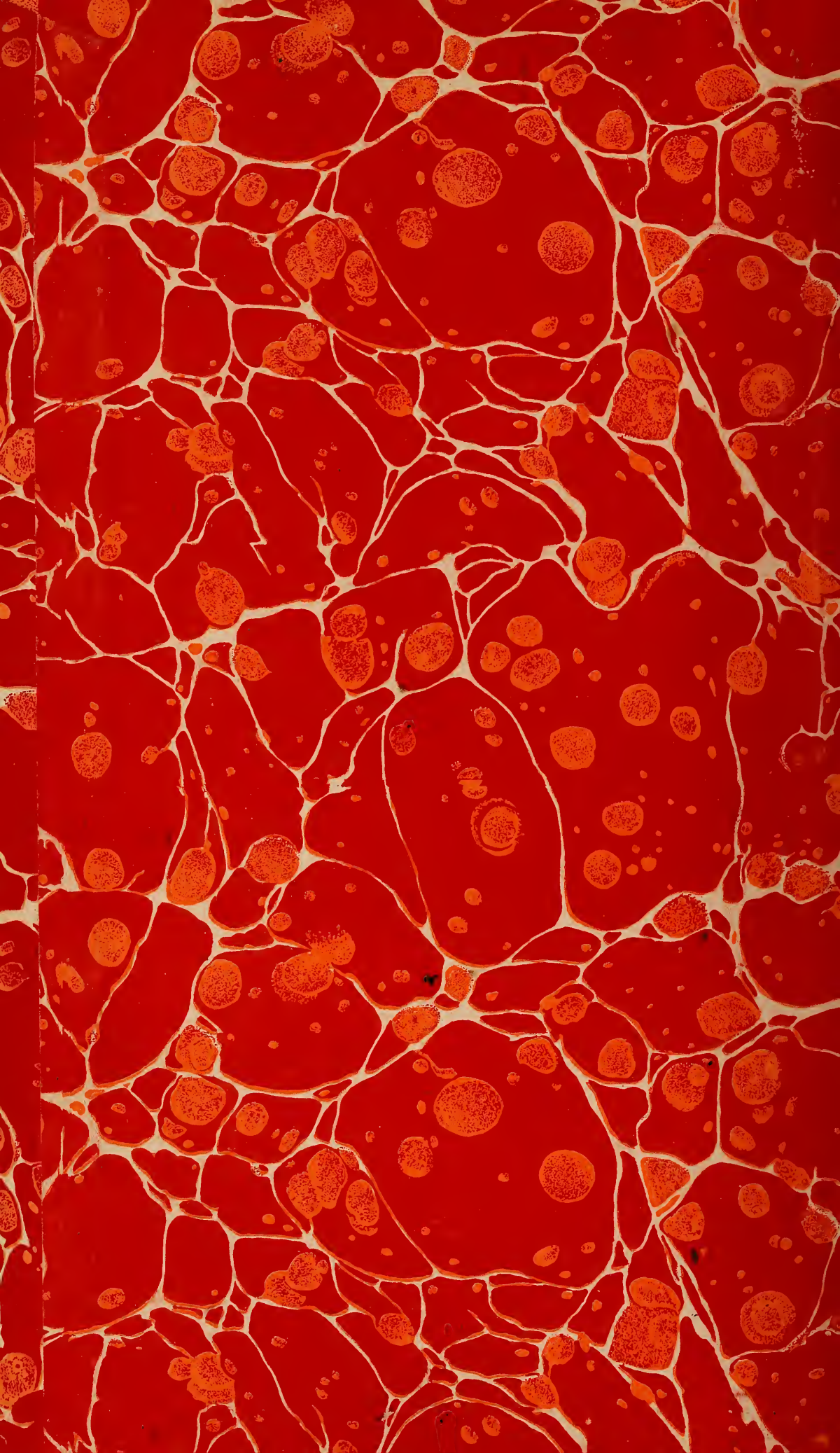
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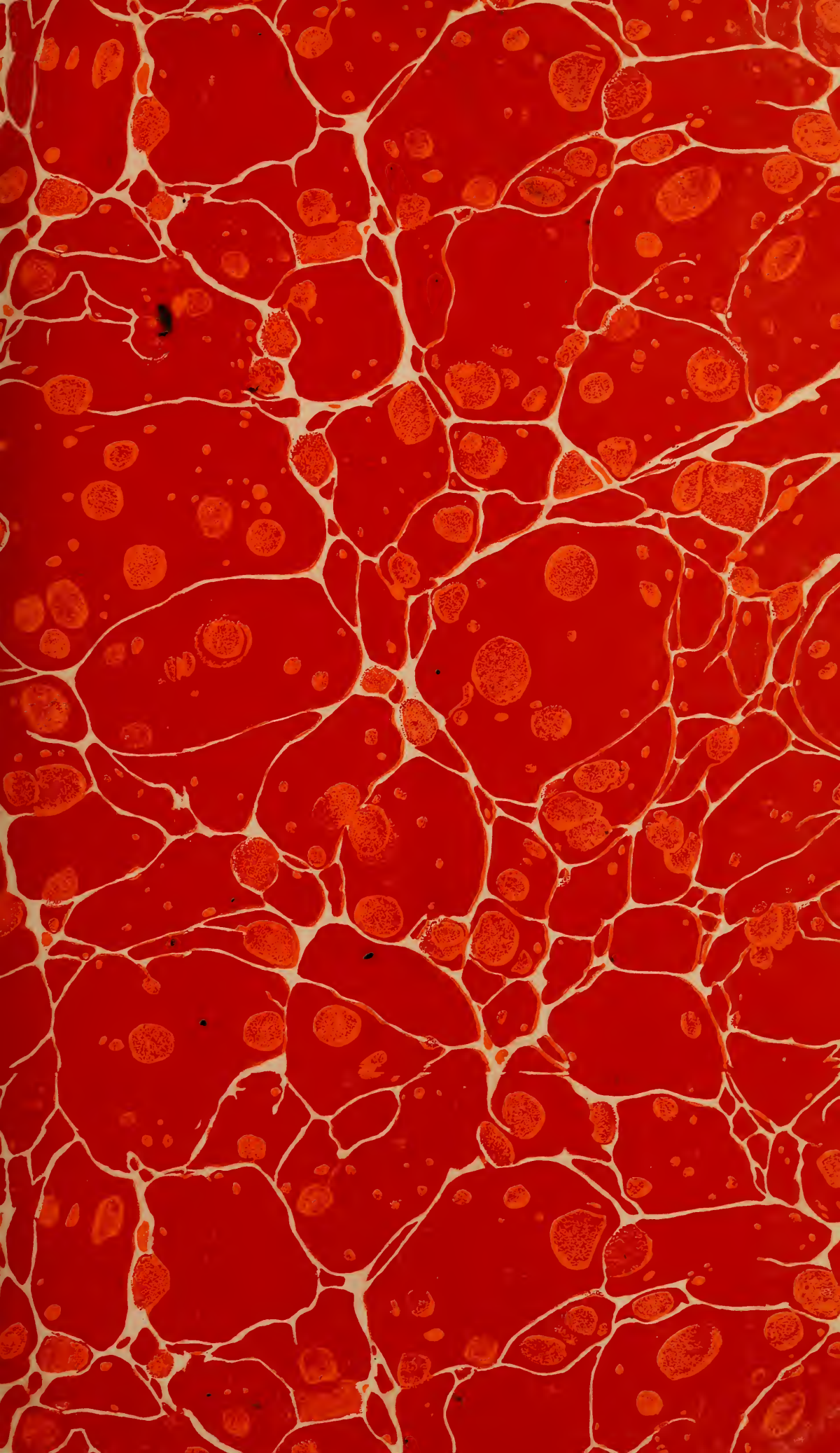


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BUREAU OF STANDARDS JOURNAL OF RESEARCH

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ISOLATION OF THE THREE XYLENES FROM AN OKLAHOMA PETROLEUM¹

By Joseph D. White² and F. W. Rose, jr.²

ABSTRACT

Each of the three xylenes has been isolated in a high state of purity from an Oklahoma petroleum. The relative amounts present are *o*, 3; *m*, 3; *p*, 1, the total xylene content of the crude oil being about 0.3 per cent. The density, refractive index, boiling point, freezing point, and infra-red absorption spectrum have been determined for each xylene.

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I. INTRODUCTION

The presence of xylene in petroleum was first recognized by de La Rue and Müller.³ Since then many investigators have reported the presence of *m*-xylene, and two have reported *p*-xylene in European and Asiatic petroleum,⁴ but in no case were the hydrocarbons themselves isolated.

In the first allusion to the occurrence of aromatic hydrocarbons in American petroleum,⁵ no reference was made to the presence of xylene. Many years later, Mabery⁶ established the presence of *m*- and *p*-xylene in the oils of Ohio and Canada and also in those of California⁷ by isolating their nitro derivatives from the fraction distilling between 137° and 140° C. Not until recently, however, has *o*-xylene been detected in any petroleum. Tausz,⁸ by oxidizing the xylene fraction of a number of oils (including one from Pennsylvania), succeeded in isolating the three phthalic acids. No one, however, has reported heretofore the separation of each of the xylenes from petroleum.

¹ Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project No. 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

² Research associate representing the American Petroleum Institute.

³ Warren de La Rue and Hugo Müller, Proc. Roy. Soc., vol. 8, p. 221, 1856.

⁴ Engler-Höfer, Das Erdöl, vol. 1, pp. 361-362, Hirzel, Leipzig, 1913; and the references there cited.

⁵ C. Schorlemmer, Chem. News, vol. 7, p. 157, 1863.

⁶ C. F. Mabery, Proc. Am. Acad. Arts Sci., vol. 31, p. 35, 1895.

⁷ C. F. Mabery and E. J. Hudson, Proc. Am. Acad. Arts Sci., vol. 36, p. 261, 1901.

⁸ J. Tausz, Zeit. angew. Chem., vol. 32 (I), p. 361, 1919.

This paper describes the isolation of these three hydrocarbons from an Oklahoma petroleum.⁹ Separation of the three isomers from a highly concentrated mixture of the xylenes was accomplished by first extracting with liquid sulphur dioxide the fraction in which the xylenes collected during distillation and then subjecting the extract to systematic crystallization alternated with distillation. *m*-Xylene was also isolated from a eutectic mixture of the *m*- and *p*-isomers by sulphonation and hydrolysis.

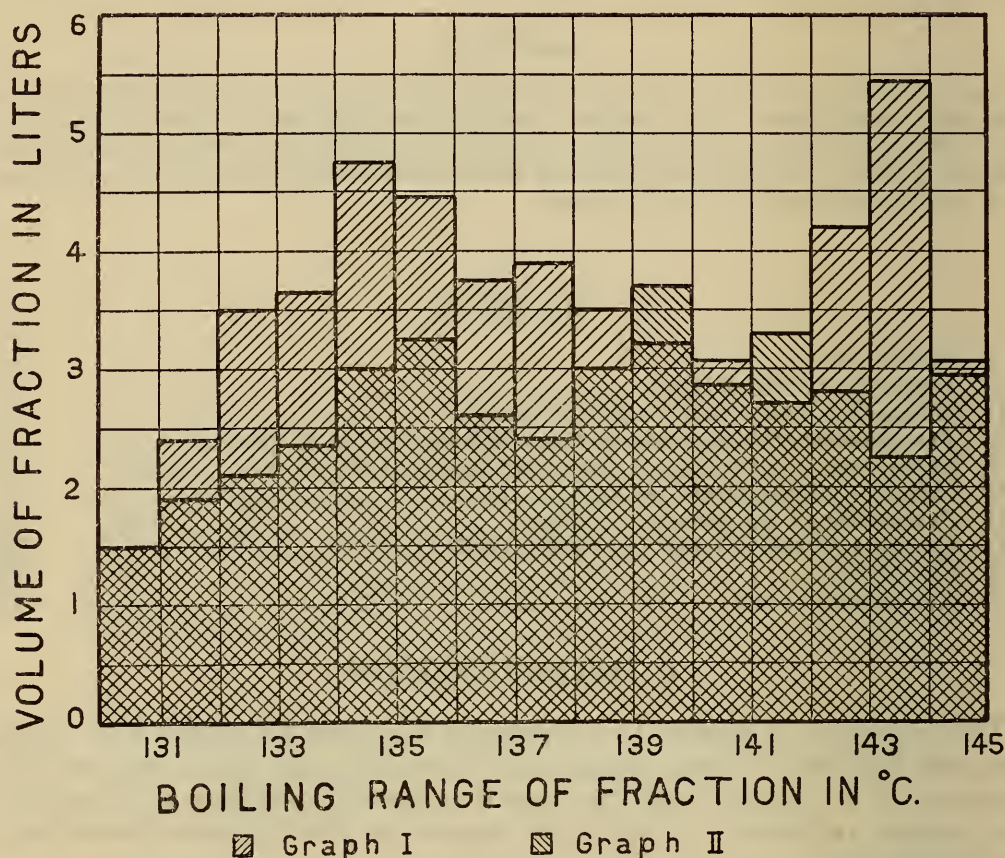


FIGURE 1.—Distribution of volume of the fractions boiling between 130° and 145° C

Graph I, before extraction with liquid sulphur dioxide; Graph II, after extraction and subsequent fractional distillation

II. PRELIMINARY DISTILLATION

The petroleum, which had received a preliminary distillation in an oil refinery, was fractionated further with the aid of efficient rectifying columns¹⁰ in the manner described elsewhere.¹¹ Nearly 45 liters of distillate collected within the temperature range of 127° to 141° C. The distribution by volume of the majority of this fraction with respect to the boiling range is shown by Graph I, in Figure 1. An examination of the 1° cuts of this distillate showed a variation in

⁹ For description and properties of the petroleum see E. W. Washburn, J. H. Bruun, and M. M. Hicks, B. S. Jour. Research, vol. 2, p. 469, Table 1, 1929.

¹⁰ (a) E. W. Washburn, J. H. Bruun, and M. M. Hicks, B. S. Jour. Research, vol. 2, p. 470, 1929.

(b) R. T. Leslie and S. T. Schickltanz, B. S. Jour. Research, vol. 6, p. 378, 1931.

(c) J. H. Bruun and S. T. Schickltanz, B. S. Jour. Research, vol. 7, p. 851, 1931.

¹¹ J. D. White and F. W. Rose, B. S. Jour. Research, vol. 7, p. 907, 1931.

refractive index of $n_D^{20} = 1.420$ to 1.443 , with a maximum value for the distillate boiling between 136° and 137° C. The high refractive indices, together with the characteristic odor of the material, strongly suggested the presence of aromatic hydrocarbons. Cooling curves showed that the fraction distilling between 134° and 136° C., which

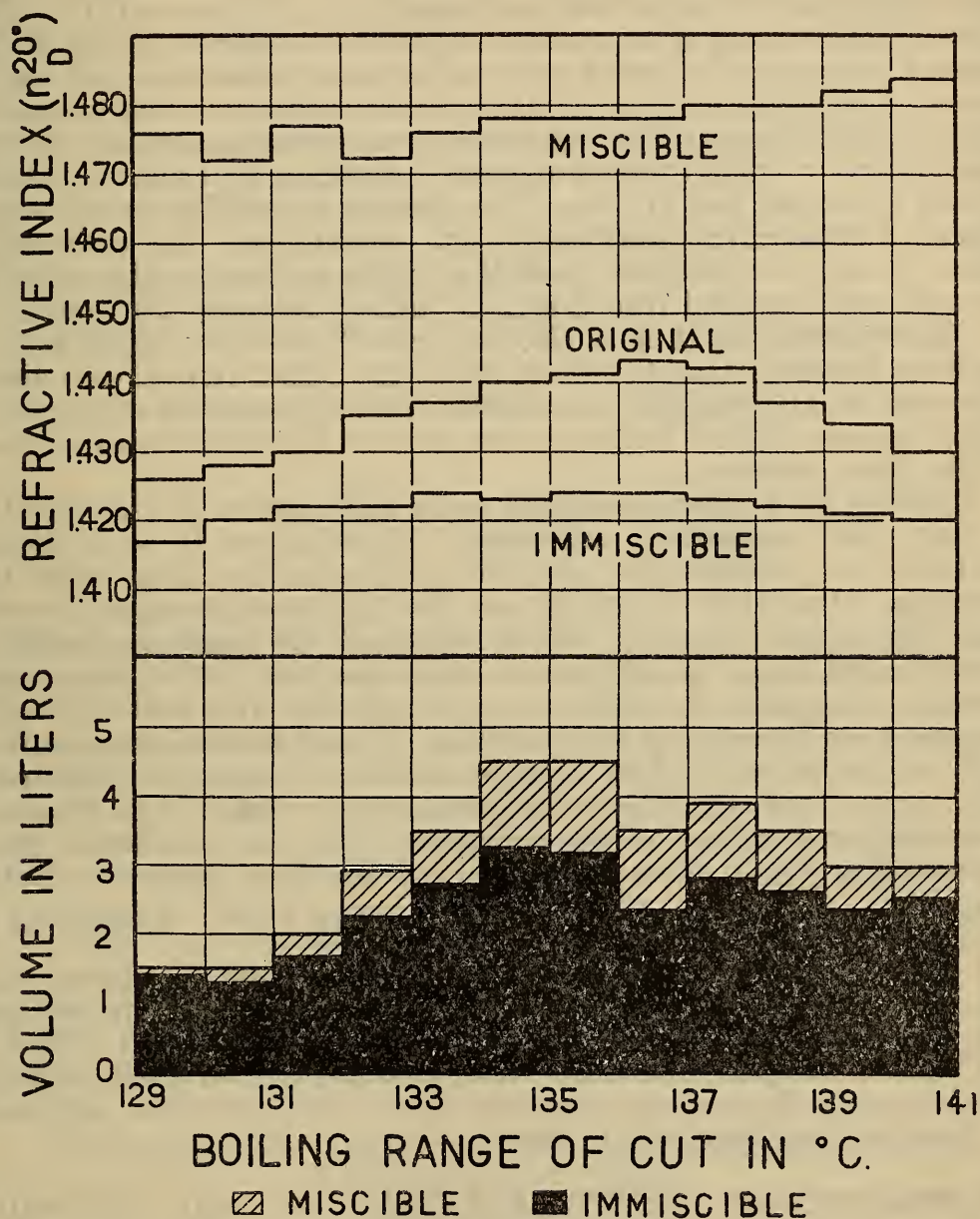


FIGURE 2.—Change in volume and refractive index of distillation fractions upon extraction with liquid sulphur dioxide

was the largest, had an initial freezing point of about -80° C. Its behavior on cooling indicated that it might be fractionated further by crystallization. Attempts to fractionate it in this manner resulted in some separation, but not enough to warrant adoption of this method.

III. EXTRACTION WITH LIQUID SULPHUR DIOXIDE

A more promising method for the separation of aromatic hydrocarbons from the distillate was that of extraction with liquid sulphur dioxide.¹² Small samples of a few of the 1° cuts boiling within a range which included the boiling points of ethylbenzene and the xylenes were extracted with liquid sulphur dioxide at -35° to -40° C. The high refractive index of the extract and the low refractive index of the immiscible portion indicated that pronounced separation had taken place. Accordingly, about 40 liters of the distillate boiling between 127° and 141° C. was extracted at an average temperature of -35° C. with the aid of the extraction apparatus designed by Leslie.¹³ About 9 liters of extract and 31 liters of immiscible material were obtained. Figure 2 illustrates graphically the results of the extraction. There it may be observed that the major portion of the miscible material was obtained from fractions boiling between 134° and 139° C. It is interesting to note also in Figure 2 that the higher boiling fractions yielded extracts with increasingly higher refractive indices. This may be attributed to a probable greater proportion of *o*-xylene, which has the highest boiling point and the highest refractive index of the three xylenes.

Treating the immiscible portion again with sulphur dioxide resulted in very little additional extraction. Nevertheless it was deemed advisable to redistill this material systematically along with the fractions of the crude oil boiling over the temperature ranges immediately below and above it, and to reextract the resulting distillate. Before redistilling, the sulphur dioxide dissolved in the immiscible fraction was removed, first by sweeping it out with carbon-dioxide gas and then by shaking the gas-swept oil with pulverized soda lime until the odor of sulphur dioxide could no longer be detected.¹⁴ The result of the redistillation is illustrated by Graph II in Figure 1. The refractive indices of the fractions from this distillation were considerably lower than those for the fractions from the initial distillation. In no case was n_D^{20} greater than 1.430. Extraction of

the 42-liter portion distilling between 128° and 144° C. yielded only 3.3 liters of extract. As before, the major portion of this material was obtained from the fractions boiling between 134° and 139° C.¹⁵

The two samples of extract were combined, freed from sulphur-dioxide gas in the manner described above, and were then subjected to fractionation by crystallization.

IV. FRACTIONAL CRYSTALLIZATION OF THE SULPHUR DIOXIDE EXTRACT

A study of the behavior of the extract upon cooling showed that the fractions with the higher refractive indices could be readily

¹² For further study of the merits and technic of extracting petroleum with liquid sulphur dioxide, see

(a) L. Edeleanu, *Trans. Am. Inst. Min. Eng.*, vol. 93, p. 2313, 1914.

(b) S. E. Bowrey, *Pet. Rev.*, vol. 36, p. 351, 1917.

(c) R. L. Brandt, *Jour. Ind. Eng. Chem.*, vol. 22, p. 218, 1918.

(d) R. J. Moore, J. C. Morrell, and G. Egloff, *Met. Chem. Eng.*, vol. 18, p. 396, 1918.

(e) J. Tausz and A. Stüber, *Zeit. angew. Chem.*, vol. 32 (I), p. 175, 1919.

(f) R. T. Leslie, *B. S. Jour. Research*, vol. 8, p. 591, 1932.

¹³ R. T. Leslie, *B. S. Jour. Research*, vol. 8, p. 591, 1932.

¹⁴ Experience showed that in the presence of even a trace of sulphur dioxide considerable decomposition of the oil took place on heating.

¹⁵ This observation is of interest in view of the fact that *o*-xylene, which was later found to comprise a fourth of the extract, boils at approximately 144° C.

crystallized in a bath cooled with solid carbon dioxide. The fractions with lower refractive indices yielded no crystals at the sublimation temperature of solid carbon dioxide, but did crystallize when cooled further (to about -90° C.) with liquid air. These promising results made it seem advisable to subject the material to further fractionation by equilibrium melting and accordingly this was done by a method described elsewhere.¹⁶ The melted oil was collected in successive cuts which were preserved according to their refractive indices and melting points. For observing the temperature trend during freezing and melting a toluene thermometer, or a single-junction thermocouple of copper constantan, was kept immersed in the oil during operations.

Systematic fractionation in this manner resulted finally in a series of fractions grouped according to Table 1.

TABLE 1.—Fractions obtained by crystallizing the sulphur-dioxide extract

Fraction	Volume	n_D^{20}	Crystallizing range
	<i>ml</i>		$^{\circ}$ C.
1	5,500	1.495 to 1.500	-50 to -65
2	1,425	1.485 to 1.495	-65 to -80
3	400	1.475 to 1.485	-80 to -90
4	1,750	1.470 to 1.475	-90 to -100

The remainder of the original 12.5-liter portion consisted of mother liquor with $n_D^{20}=1.470$ and with a crystallizing range from -100° to -125° C. Its fractionation by crystallization could be accomplished only with difficulty and resulted in but little separation. Therefore it was extracted again with liquid sulphur dioxide. The extract had the following properties; $n_D^{20}=1.483$, B. P. = 136° C., F. P. = -96° C. These properties, as well as its characteristic odor, indicated that the material was impure ethyl benzene. Work is now in progress on its isolation. The immiscible portion has been preserved also. Its physical properties indicate that it is probably a mixture of naphthenes and iso-nonanes. It should be pointed out that fractional crystallization of the original sulphur dioxide extract served to separate the major portion of these impurities from the xylenes, which concentrated in the "crystal fraction."

V. SYSTEMATIC DISTILLATION OF THE CRYSTALLIZATION FRACTIONS

Oxidation of samples of the crystal fractions, with neutral potassium permanganate, yielded the three phthalic acids. This fact, together with the observed refractive index and the crystallization range, and the further observation that the major portion of the material distilled between 138° and 144° C., indicated that it was a mixture of *p*-, *m*-, and *o*-xylene.

With the aid of the rectifying columns used in the earlier distillations, separate portions of the mixture were fractionally distilled under atmospheric pressure and under a pressure of 215 mm Hg. The distribution of the volumes of the fractions with respect to their

¹⁶ R. T. Leslie and S. T. Schick Tanz, B. S. Jour. Research, vol. 6, p. 378, 1931. The apparatus used in this work is illustrated on p. 382 of the reference cited.

boiling range indicated that better fractionation resulted under the reduced pressure. As a consequence the entire mixture of xylenes was subjected to a systematic distillation at a pressure of 215 mm Hg, and was finally separated into two fractions. One of these, consisting of about 2 liters and boiling normally near 144° C., appeared from its behavior on freezing to be impure *o*-xylene. The other portion (a 3-liter fraction) boiling between 138° and 139° C. was found in the same manner to be chiefly a mixture of *p*-, and *m*-xylene.

VI. ISOLATION OF THE THREE XYLENES

The 2-liter fraction of *o*-xylene was further purified by fractional crystallization. With the aid of a centrifuge which could be operated at low temperatures ¹⁷ good separation of crystals from mother liquor was attained. As a result of this fractionation a sample of *o*-xylene was isolated, the physical properties of which (see below) indicated it to be of high purity.

Fractional crystallization of the distillate containing the *p*- and *m*-xylene separated it into a *p*-xylene fraction and into a mixture of the two isomers approximating their eutectic in composition. Further fractionation by crystallization of the material rich in *p*-xylene yielded a very pure sample of this hydrocarbon. (See Table 4.)

Systematic crystallization of the impure eutectic mixture resulted in the separation of a crystal fraction which froze at a constant temperature of -55° C. This freezing point agreed well with the value recorded by Nakatsuchi ¹⁸ for the freezing point of a synthetic eutectic mixture of *p*- and *m*-xylene. The identity of this material was definitely established by comparing its properties with those of a eutectic mixture of the two isomers, made by mixing them in the proportions prescribed by Nakatsuchi.

By alternating distillation with crystallization as required, a systematic fractionation of the eutectic mixture, in which cuts were made to accord with refractive index and freezing point, resulted in the isolation of a small sample of *m*-xylene. This sample is designated in Table 3 as "best by physical means." ¹⁹

One other sample of *m*-xylene was isolated from the eutectic mixture by sulphonating it at 0° C. Twice the equivalent amount of concentrated sulphuric acid ($d=1.84$) was slowly added to the oil over a period of 6 to 12 hours, during which time the mixture was constantly stirred while surrounded by an ice bath. Reaction was allowed to continue at this temperature for a total of 24 hours, at the end of which time the acid layer was separated, mixed with an equal volume of dilute sulphuric acid (1 : 1 by volume) and steam distilled. Hydrolysis took place most effectively at 130° to 135° C., although to some extent below and above this temperature range. ²⁰ Nearly pure

¹⁷ M. M. Hicks-Bruun and J. H. Bruun, B. S. Jour. Research, vol. 8, p. 523, 1932.

¹⁸ A. Nakatsuchi, J. Soc. Chem. Ind., Japan, vol. 29, p. 29, 1926.

¹⁹ The difficulty of isolating *m*-xylene from its eutectic mixture with *p*-xylene may be appreciated from the fact that the major portion of the mixture distills at substantially a constant temperature, viz, 138.6° to 138.7° C. The residue remaining in the still at the end of the distillation is, however, somewhat richer in *m*-xylene. Moreover, the eutectic mixture contains 85 parts by weight of *m*-xylene and freezes only 7° below the freezing point of that component.

²⁰ For further study of sulphonation and hydrolysis as a means for separating and analyzing xylene mixtures see: (a) O. Jacobsen, Ber., vol. 10, p. 1009, 1877. (b) J. M. Crafts, Compt. rend., vol. 114, p. 1110, 1892. (c) H. T. Clarke and E. R. Taylor, J. Am. Chem. Soc., vol. 45, p. 830, 1923. (d) T. S. Patterson, A. McMillan, and R. Somerville, J. Chem. Soc., vol. 125, p. 2488, 1924. (e) N. Kishner and G. Vendelshtein, J. Russ. Phys. Chem. Soc., Chem. Part, vol. 57, p. 1, 1926. (f) A. Nakatsuchi, J. Soc. Chem. Ind., Japan, vol. 32, Suppl. Binding, p. 335, 1929.

m-xylene was thus obtained, which upon fractional crystallization yielded a sample of *m*-xylene of very high purity. This sample is designated in Table 3 and Figure 4 as "best by sulphonation."

VII. PROPERTIES OF THE ISOLATED XYLENES

To establish the identity of the isolated xylenes, the purest sample of each was selected on the basis of its behavior on freezing, and the physical properties of each of these were compared with the physical properties of the corresponding synthetic xylene reported in the literature. In addition, a similar comparison was made in the case of *m*-xylene and *p*-xylene, with samples obtained from the Bureau des Étalons Physico-Chimiques in Brussels. These highly pure samples were prepared by J. Timmermans and his coworkers. The results of these comparisons are tabulated in Tables 2, 3, and 4. The density measurements were made by the Division of Weights and Measures of this Bureau. The other properties were determined by the writers. Refractive indices were measured with a calibrated Abbé refractometer (Valentine design) under well-controlled temperature conditions. Readings could be readily made to within two units in the fifth decimal place and the values listed are estimated to be correct to within ± 0.00005 . Boiling points were determined in a Cottrell boiling-point apparatus. During the process the entire mercury thread of the thermometer was surrounded by the condensing vapors. Freezing points were determined either with a platinum resistance thermometer or a 5-junction thermocouple calibrated against the thermometer. It is believed that the values reported are correct to within ± 0.02 .

TABLE 2.—Comparison of the physical constants of *o*-xylene from petroleum with previously reported constants of synthetic *o*-xylene

Sample	d_{4}^{27}	d_{4}^{20}	n_D^{25}	Boiling point, 760 mm Hg	Freezing point (in dry air)
From petroleum.....	¹ 0.87445	² 0.88040	¹ 1.50301	^{°C.} 144.4	^{°C.} ³ -25.30
Synthetic (previously reported).....	⁴ 874	⁴ 880	⁴ 1.5033	^{°C.} ⁵ 144	^{°C.} ⁶ -25.74

¹ ± 0.00001 . Determined by the section of capacity and density of this bureau.
² Calculated from value determined at 27° C., assuming the same temperature coefficient as for *m*-xylene.
³ Determined with platinum resistance thermometer.
⁴ K. Von Auwers, Ann., vol. 419, p. 92, 1919. Calculated from values given for 20° C.
⁵ Int. Crit. Tables, vol. 1, p. 219 (McGraw-Hill Book Co., 1926).
⁶ A. Nakatsuchi, J. Soc. Chem. Ind., Japan, vol. 32, Suppl. Binding, p. 333; 1929.

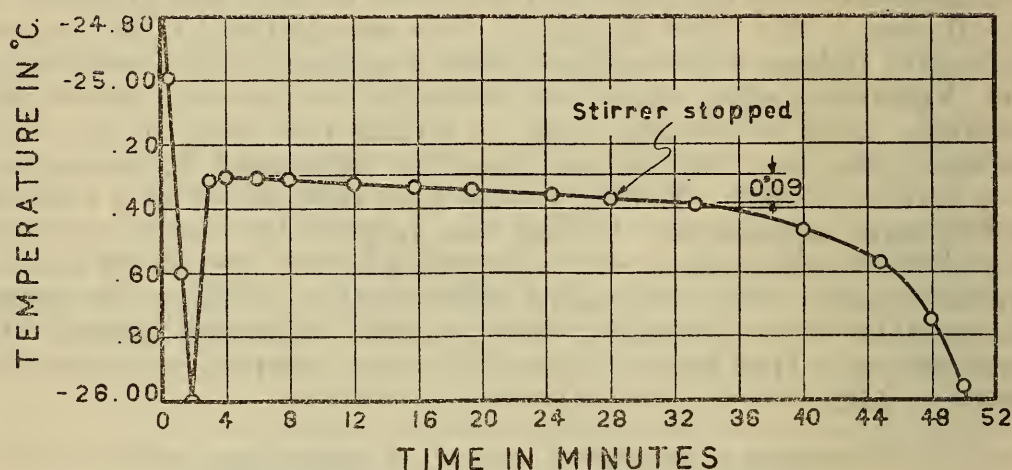
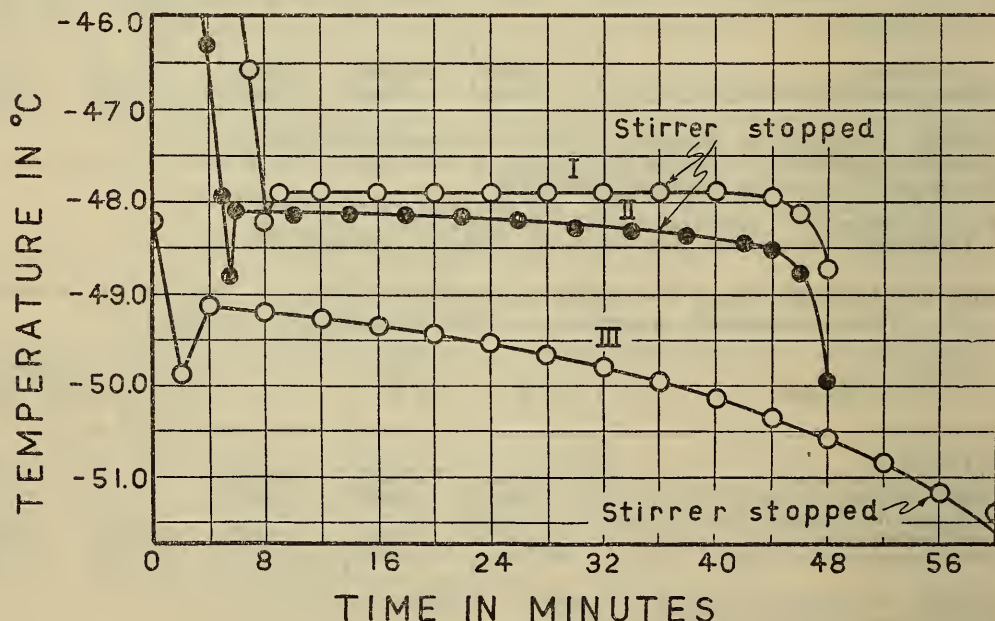
TABLE 3.—Comparison of the physical constants of certain samples of *m*-xylene with previously reported constants of synthetic *m*-xylene

Sample	d_{4}^{27}	d_{4}^{20}	n_D^{25}	Boiling point 760 mm Hg	Freezing point (in dry air)
From petroleum:				^{°C.}	^{°C.}
Best by sulphonation.....	¹ 0.85817	² 0.86412	1.49467	139.15	³ -47.89
Best by physical means.....	1.85821	² 86416	1.49468	139.15	-49.13
From Bureau des Étalons Physico-Chimiques (Timmermans).....	1.85821	² 86416	1.49467	139.15	³ -48.05
Synthetic (previously reported).....	⁴ 85806	⁴ 86401	⁶ 1.4948	⁴ 139.30	⁴ 7 -47.55

¹ ± 0.00001 . Determined by the section of capacity and density of this bureau.
² Calculated from values determined at 27° C.
³ Determined with platinum resistance thermometer.
⁴ J. Timmermans, J. chim. phys., vol. 27, p. 402, 1930.
⁵ Calculated from value given for 30° C.
⁶ Int. Crit. Tables, vol. 1, pp. 219, 277 (McGraw-Hill Book Co.), 1926. Calculated from value given for 20° C.
⁷ Recent value given in a private communication from Dr. Timmermans.

TABLE 4.—Comparison of the physical constants of certain samples of *p*-xylene with previously reported constants of synthetic *p*-xylene

Sample	d_{4}^{27}	d_{4}^{20}	n_D^{25}	Boiling point 760 mm Hg	Freezing point (in dry air)
From petroleum-----	¹ 0.85498	² 0.86107	1.49320	°C. 138.4	°C. ³ 13.21
From Bureau des Étalons Physico-Chimiques (Timmermans)-----	1.85509	2.86118	1.49320	138.4	³ 13.21
Synthetic (previously reported)-----	⁴ 5.85491	⁴ 5.86100	⁴ 5.1.49370	⁴ 138.40	⁴ 13.35 ⁶ 13.19

¹ ± 0.00001 . Determined by the section of capacity and density of this bureau.² Calculated from values determined at 27° C.³ Determined in this bureau by B. J. Mair with a platinum resistance thermometer.⁴ J. Timmermans, J. chim. phys., vol. 23, p. 756, 1926.⁵ Calculated from values given for 15° C.⁶ A. Nakatsuchi, J. Soc. Chem. Ind., Japan, vol. 32, Suppl. Binding, p. 333, 1929.FIGURE 3.—The time-temperature freezing curve of *o*-xylene isolated from petroleumFIGURE 4.—Freezing curves of *m*-xylene

Curve I, from petroleum, best by sulphonation; Curve II, from Bureau des Étalons Physico-Chimiques; and Curve III, from petroleum, best by physical means

As a test of purity of the samples of the isolated hydrocarbons, their behavior during freezing was determined. Figure 3 shows the time-temperature cooling curve of *o*-xylene isolated from petroleum,

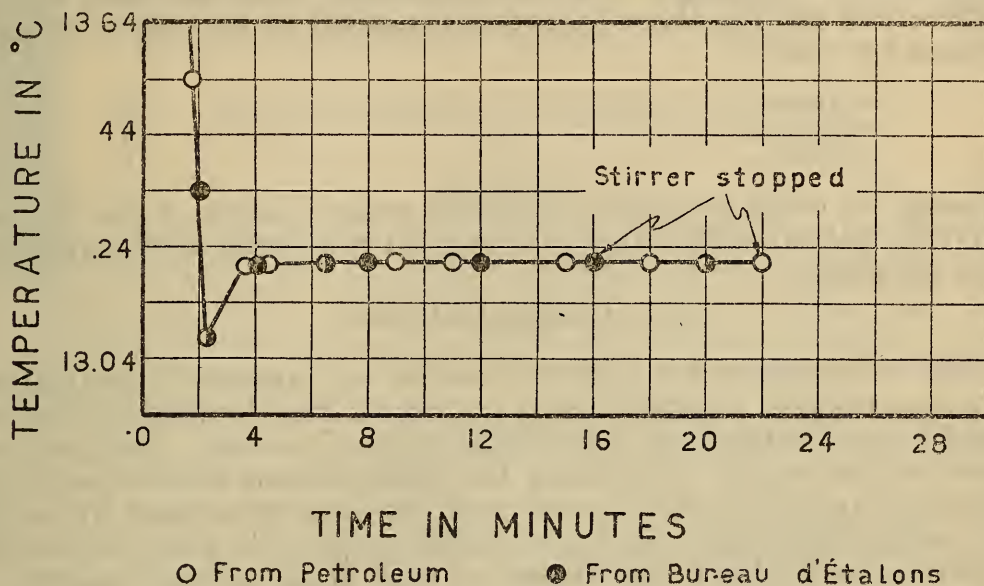


FIGURE 5.—Freezing curves of *p*-xylene

while Figures 4 and 5 show similar curves for the several samples of *m*- and *p*-xylene which include those isolated from petroleum. The very narrow temperature range during the course of freezing (shown by the slope of the flattened portion of the curves) indicates that the

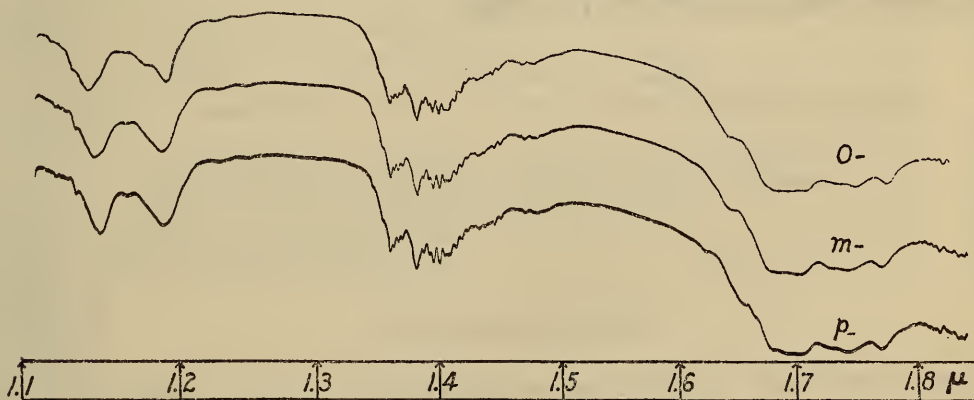


FIGURE 6.—Infra-red absorption spectra of the xylenes

Energy transmission curves showing the infra-red absorption spectra of the three isomeric xylenes in 4 mm cell depth from the emission of a tungsten filament lamp. The broad bands from 1.65 μ to 1.76 μ and 1.14 μ to 1.21 μ are the first and second overtones, respectively, of the fundamental hydrocarbon vibration frequency at 3.3 to 3.4 μ . The sharp, peaked absorption bands are due to atmospheric water-vapor in the light-path of the spectrograph. The bands at 1.14 and 1.19 show the clear differentiation in the absorption of the aromatic and aliphatic C \leftrightarrow H vibration; the 1.14 μ band being due to the nuclear C-H absorption, and the 1.19 μ band, the absorption of the side-chain C-H. Slit-width approx. 20 A.

best samples are in a state of high purity. Figure 6 shows the infra-red absorption spectra of the isolated xylenes. The spectra were recorded by U. Liddel, of the Fixed Nitrogen Research Laboratory, Bureau of Chemistry and Soils.

VIII. CONTENT OF THE XYLENES IN THE CRUDE OIL

Analysis of the various xylene fractions by the freezing-point method (thermal analysis) shows that, based upon the total xylene in the crude oil, the three isomers are present in the following proportions by weight:

<i>o</i> -xylene.....	3
<i>m</i> -xylene.....	3
<i>p</i> -xylene.....	1

Allowing for losses incurred during the various stages of the separation, it is estimated that the total amount of xylenes in the crude oil is 0.3 per cent.

IX. CONCLUSIONS

This investigation confirms the results of previous investigators that the aromatic constituents of petroleum may be readily concentrated by extracting them with liquid sulphur dioxide. This method serves well as an aid in isolating the hydrocarbons themselves from petroleum and is superior to the usual chemical treatment by nitration, which, because of the large number of possible products, would be unsuitable for the determination of each of the xylenes present.

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